Synthesis and Crystal Structure of Co(III) Dioximates with the Complex Anion [SbF₆]⁻

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Abstract—The complexes $[Co(DioxH)_2L_2][SbF_6] \cdot nH_2O$, where DioxH is dimethylglyoxime monoanion $(DioxH^-)$ or 1,2-cyclohexanedione dioxime $(NioxH^-)$, L is aniline (An) or triphenylphosphine (PPh_3) , were isolated from the $CoX_2 \cdot nH_2O$ —NaSbF₆—DioxH₂—L system (X = F or CH₃COO) in aqueous methanol. The complexes were studied by UV, IR, and NMR spectroscopy and by X-ray diffraction. The crystal structure of $[Co(DH)_2(An)_2][SbF_6] \cdot H_2O$ (I) and $[Co(NioxH)_2(PPh_3)_2][SbF_6]$ (II) is stabilized by the electrostatic interactions between the Co(III) complex cations and outer-sphere fluorine-containing anions and by hydrogen bonds between structural units.

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Transition metal compounds of α -dioximes form a broad field of coordination chemistry. Their diversity is caused by the nature of the metal used, the type of dioxime, and additional organic ligands and anions. The dioxime compounds can also differ by structural features because α -dioximates can be prepared as complex cations or molecular complexes and can be monomeric, dimeric, or polymeric. The interest in these compounds has been revived in recent years due to their physical and chemical properties, which can account for their applications in analytical chemistry, extraction processes, magnetic materials, or models of biological systems [1-5]. A crucial factor of the synthesis of transition metal complexes with α -dioximes is the formation of stable chelates. The diversity of the obtained Co(III) complexes is determined by both the conditions of synthesis and the nature of the additional ligands and anions. The conditions for variation of their composition and structure and for gaining new properties are mainly related to the use of ligands axially coordinated to the metal atom [1-3].

In recent years, we have focused attention on the study of *trans*-octahedral cobalt(III) dioximates incorporating F⁻, $[H_2F_3]^-$ and various fluorine-containing anions ($[BF_4]^-$, $[SiF_5]^-$, $[CF_3SO_3]^-$, $[SiF_6]^{2-}$, $[BeF_4]^{2-}$, $[ZrF_6]^{2-}$, $[TiF_6]^{2-}$, $[AIF_6]^{3-}$) [6–16]. The anions with different steric capacity differ by the number of atoms that are able to function as hydrogen bond acceptors and, as a consequence, affect the mode of packing of components into the crystal. Cobalt(III) compounds with hexafluoroantimonate ion have been

reported [17, 18]; but complexes with α -dioximes were synthesized for the first time.

The complexes $[Co(DioxH)_2L_2][SbF_6] \cdot nH_2O$, where DioxH⁻ is the dimethylglyoxime monoanion (DH⁻) or 1,2-cyclohexanedione dioxime (NioxH⁻), and L is aniline (An) or triphenylphosphine (PPh₃), were obtained from the CoX₂ · nH_2O -NaSbF₆-DioxH₂-L system (X = F or CH₃COO) in CH₃OH-H₂O. The composition and structure of these compounds were studied by spectroscopy and by X-ray diffraction, which was used for unambiguous determination of the molecular and crystal structures of $[Co(DH)_2(An)_2][SbF_6] \cdot H_2O$ (I) and $[Co(NioxH)_2(PPh_3)_2][SbF_6]$ (II).

EXPERIMENTAL

Synthesis of I. A solution of NaSbF₆ (0.26 g, 1 mmol) in water (10 mL) was added to a solution of $CoF_2 \cdot 4H_2O$ (0.17 g, 1 mmol) in hot water (10 mL), and the mixture was heated to ~70°C. Then a mixture of dimethylglyoxime (0.23 g, 2 mmol) in methanol (30 mL) and aniline (1 mL) was added dropwise. The reaction mixture was kept at a specified temperature for 10–15 min being oxidized by air oxygen. The brown solution was filtered and left for slow evaporation at room temperature. Dark brown prismatic crystals precipitated. Yield ~20%. The compound was soluble in DMF, DMSO, and alcohols and less soluble in water.

Synthesis of II. 1,2-Cyclohexanedione dioxime (0.28 g, 2 mmol) and PPh₃ (0.52 g, 2 mmol) were dissolved in methanol (50 mL). The solution was heated on a water bath to ~ 60° C. An aqueous solution of Co(CH₃COO)₂ · 4H₂O (0.25 g, 1 mmol) and NaSbF₆ (0.26 g, 1 mmol) was added dropwise to the mixture of ligands in such a way that the temperature of the reaction mixture did not drop sharply. The final solution was heated with a reflux condenser for 1 h, filtered, and left for slow evaporation at room temperature. Brown prismatic crystals precipitated from the solution. Yield ~22%. The compound was soluble in DMF, DMSO, and alcohols and less soluble in water.

IR spectra of complexes of I and II were recorded on a 100 FT-IR spectrometer in mineral oil at 4000– 400 cm⁻¹ and ATP at 4000–650 cm⁻¹. UV spectra were measured on a Lambda 25 Perkin Elmer spectrophotometer for aqueous solutions $(0.5 \times 10^{-4} \text{ mol/L})$. The ¹⁹F NMR spectra of $[Co(DH)_2(An)_2][SbF_6]$ · H₂O were measured on a Bruker-300 MHz spectrometer in D₂O using CFCl₃ as the internal standard.

X-Ray diffraction study of I and II was performed at room temperature on a STOE IPDS diffractometer (Mo K_{α} radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω scan mode). The crystal structures were solved by the direct method and refined by the leastsquares method in the anisotropic full-matrix approximation for non-hydrogen atoms (SHELX-97) [19]. The positions of the oxime and water hydrogen atoms were found from the difference Fourier maps, the other were calculated geometrically and refined isotropically in the rigid body model. The crystal data and X-ray experiment details for I and II are summarized in Table 1, the interatomic distances and bond angles are in Table 2, and the geometric parameters of hydrogen bonds are in Table 3. The positional and thermal parameters for structures I and II are deposited with the Cambridge Crystallographic Data Centre (nos. 828210 (I) and 828211 (II); deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk/data request/cif).

RESULTS AND DISCUSSION

The compounds I and II are ionic. The Co(III) complex cations coordinate the dimethylglyoxime (I) and 1,2-cyclohexanedione dioxime (II) residues, and the ligands An and PPh₃, respectively, are in the apical positions. The counter-ions are the $[SbF_6]^-$ anions in both compounds. The crystals of I contain crystallization water molecules.

In the UV spectrum, the band at 230–250 nm corresponds to the π - π * transition in the Co(DioxH)₂ group, while the band at 350–390 nm indicates the presence of other ligands (An, PPh₃) in the 1,6-coordinate.

The IR spectrum of complex I exhibits absorption bands at 1610 v(CN), 1240 v_{as}(NO), 1091 v_s(NO), 517 v_{as} (Co–N), and 432 cm⁻¹ v_s (Co–N), which confirmed the coordination of dimethylglyoxime to the central atom. The 742 and 685 cm⁻¹ δ (CH) absorption bands typical of a monosubstituted aromatic ring and the 3264, 3068 v(NH) and 1556 cm⁻¹ δ (NH) bands are indicative of aniline position in the apical coordinate. The presence of nioxime in complex II is proved by the presence of 1668 v(CN), 1229 v_{as} (NO), 1087 $v_{s}(NO)$, 511 $v_{as}(CO-N)$, and 427 cm⁻¹ $v_{s}(CO-N)$ bands in the IR spectrum. The presence of PPh₃ molecules in complex II is confirmed by the 2959, 2864 v(CH); 1435, 1001 v(PC); and 751, 683 cm⁻¹ $\delta(CH)$ bands, which are typical of monosubstituted aromatic ring.

The presence of outer-sphere hexafluoroantimonate ion is indicated by the ¹⁹F NMR signal at $-118.7 \text{ ppm} (\delta [\text{SbF}_6]^-)$.

The crystals of I are composed of centrosymmetric $[Co(DH)_2(An)_2]^+$ cations, $[SbF_6]^-$ anions located on a twofold axis, and H_2O in 1 : 1 : 1 ratio (Fig. 1). The Co(III) coordination polyhedron is the octahedron formed by four nitrogen atoms of two dimethylglyoxime residues located in one plane and combined by intra-ion hydrogen bonds (HB) and by two nitrogen atoms of two aniline molecules on the axial coordinates. The Co–N interatomic distances are 1.892(2), 1.900(2), and 2.012(2) Å (Table 2) and the donoracceptor distance in the O-H…O intra-ion HB is 2.518(3) Å (Table 3). The mean plane of the aniline molecules forms an 32.1° angle with the 4N equatorial plane. This arrangement of these fragments implies weak $\pi - \pi$ interactions between the An aromatic rings and the corresponding five-membered metal rings formed by DH⁻ (the distance between the centroids of the rings is 3.630 Å). In the $[SbF_6]^-$ anion, the Sb-F distances (1.884(2)-1.901(2) Å) are consistent with published data [17, 18, 20].

Along with the electrostatic interactions between the Co(III) complex cations and outer-sphere anions

	Value			
Parameter	Ι	II		
M	729.18	1101.52		
Т, К	213(2)	150(2)		
System	Monoclinic	Monoclinic		
Space group	C2/c	$P2_{1}/c$		
Unit cell parameters:				
<i>a</i> , Å	19.9183(12)	9.6182(2)		
<i>b,</i> Å	8.6607(7)	18.9886(3)		
<i>c,</i> Å	15.8740(10)	12.9557(4)		
β, deg	99.544(7)	107.256(3)		
<i>V</i> , Å ³	2700.5(3)	2259.67(9)		
Ζ	4	2		
ρ (calcd.), g/cm ³	1.794	1.619		
μ, mm ⁻¹	1.699	1.111		
<i>F</i> (000)	1456	1116		
Crystal size, mm	$0.22\times0.18\times0.08$	$0.25 \times 0.15 \times 0.10$		
Range of θ , deg	2.57-26.00	2.70-25.50		
Range of reflection indices	$-23 \le h \le 24, -10 \le k \le 10, -19 \le l \le 18$	$-11 \le h \le 11, -23 \le k \le 23, -10 \le l \le 15$		
The number of measured/independent re- flections	9382/2622 ($R_{\rm int} = 0.0522$)	$14822/4198 \ (R_{\rm int} = 0.0371)$		
Filling, %	98.5 ($\theta = 26.00$)	99.9 ($\theta = 25.50$)		
The number of reflections with $I > 2\sigma(I)$	2003	2003 2852		
The number of refined parameters	179	301		
GOOF	1.027 1.041			
$R\text{-factor}(I > 2\sigma(I))$	$R_1 = 0.0226, wR_2 = 0.0431$ $R_1 = 0.0306, wR_2 = 0.0494$			
<i>R</i> -factor (the whole array)	$R_1 = 0.0337, wR_2 = 0.0436$	$R_1 = 0.0535, wR_2 = 0.0511$		
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}, e {\rm \AA}^{-3}$	0.605, -0.330	0.394, -0.590		

 Table 1. Crystal data, X-ray experiment details, and structure refinement parameters for I and II

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	Complex cations			
Bond	<i>d</i> ,	Å		
	I	П		
$C_{0}(1) - N(1)$	1 892(2)	1.888(2)		
$C_0(1) = N(2)$	1.002(2) 1.900(2)	1.880(2) 1.882(2)		
$C_0(1) = N(2)$ $C_0(1) = N(2)/P(1)$	1.900(2)	1.002(2)		
N(1) = C(1)	2.012(2) 1.300(3)	2.3309(7) 1 306(3)		
N(1) = C(1) N(1) = O(1)	1.300(3) 1.345(3)	1.300(3) 1.335(3)		
N(1) = O(1) N(2) = O(2)	1.343(3) 1.202(2)	1.333(2) 1.207(2)		
N(2) = C(2)	1.293(3) 1.252(2)	1.297(3) 1.250(2)		
N(2) = O(2)	1.352(3)	1.359(2)		
C(1) - C(2)	1.4/3(4)	1.453(3)		
C(1) - C(4)/C(6)	1.493(4)	1.488(3)		
C(2) - C(3)	1.490(4)	1.486(3)		
Angle	ω, deg			
	I	II		
N(1)Co(1)N(2)	81.26(9)	81.42(9)		
N(1)Co(1)N(3)/P(1)	89.33(9)	92.12(6)		
N(2)Co(1)N(3)/P(1)	88.56(8)	91.33(6)		
$N(1)Co(1)N(2)^{\#1}$	98.74(9)	98.58(9)		
$N(1)Co(1)N(3)^{\#1}/P(1)^{\#1}$	90.67(9)	87.88(6)		
$N(2)Co(1)N(3)^{\#1}/P(1)^{\#1}$	91.44(8)	88.67(6)		
C(1)N(1)O(1)	121.3(2)	121.8(2)		
C(1)N(1)Co(1)	116.7(2)	115.8(2)		
O(1)N(1)Co(1)	122.0(2)	122.4(2)		
C(2)N(2)O(2)	119.3(2)	118.3(2)		
C(2)N(2)Co(1)	116.8(2)	116.9(2)		
O(2)N(2)Co(1)	123.9(2)	124.7(2)		
N(1)C(1)C(2)	112.6(2)	1132(2)		
N(1)C(1)C(4)/C(6)	122.5(2)	125.0(2)		
C(2)C(1)C(4)/C(6)	122.9(2) 124 9(3)	123.0(2) 121.7(2)		
N(2)C(2)C(1)	112.05(3) 112.6(2)	1122(2)		
N(2)C(2)C(3)	1230(2)	1255(2)		
C(1)C(2)C(3)	123.0(2) 124 4(2)	123.3(2) 122.3(2)		
	124.4(2) 122.3(2)			
Rond				
Dona				
	1	11		
Sb(1)-F(1)	1.884(2)	1.886(2)		
Sb(1) - F(2)	1.901(2)	1.895(2)		
Sb(1)-F(3)	1.884(2)	1.883(2)		
Angle	ω, deg			
	Ι	II		
F(1)Sb(1)F(2)	92.18(8)	89.31(8)		
F(1)Sb(1)F(3)	179.13(10)	89.25(9)		
F(2)Sb(1)F(3)	87.06(8)	90.13(8)		
$F(1)Sb(1)F(1)^{#2}$	88.0(1)	180		
$F(1)Sb(1)F(2)^{#2}$	91.82(8)	90.69(8)		
$F(1)Sb(1)F(3)^{#2}$	91.56(10)	90.75(9)		
$F(2)Sb(1)F(2)^{#2}$	174.43(11)	89.87(8)		
$F(2)Sb(1)F(3)^{#2}$	88.96(8)	89.87(8)		
$F(3)Sb(1)F(3)^{#2}$	88.9(2)	180		

Table 2. Selected interatomic distances and bond angles for I and II*

* Symmetry code for equivalent atoms: for I: $^{\#1}-x, -y + 1, -z + 2,$ $^{\#2}-x, y, -z + 3/2$; for II: $^{\#1}-x + 1, -y, -z, ^{\#2}-x + 2, -y, -z + 1.$ (Table 3, Fig. 2), the inter-ion hydrogen bonds between them and also with water molecules substantially contribute to the formation of crystal structure **I**. The NH₂ groups of the coordinated aniline molecules of the complex cations form the inter-ion HB with the F(2) atom of the $[SbF_6]^-$ anions (N…F 2.990(3) Å) and with oxygen of the crystallization water molecule (N…O(1w) 2.984(3) Å). In turn, the water molecule forms the O(1w)–H…O inter-ion HB with the oxime oxygen atom of the complex cation (O…O 2.934(2) Å) and the O(1w)–H…F inter-ion HB with the $[SbF_6]^$ anion (O…F 3.101(3) Å). The crystal of **I** also contains weak C–H…F inter-ion HB between the phenyl group of the An cation and the anion (C(8)…F(1) 3.402 Å).

The crystals of compound II are composed of centrosymmetric [Co(NioxH)₂(PPh₃)₂]⁺ cations and the $[SbF_6]^-$ anions (Fig. 3). The equatorial plane of the complex cation accommodates two 1,2-cyclohexanedione dioxime residues, while two triphenylphosphine molecules are located in the apical coordinates. The Co(III) coordination polyhedron is formed by four nitrogen atoms of two NioxH- ligands and two phosphorus atoms of PPh₃. The monodeprotonated NioxH⁻ ions are combined by two intra-ion HB (O···O 2.539(2) Å). The cyclohexane moiety of the NioxH⁻ ligand is in the half-chair conformation with the C(4)and C(5) atoms being shifted by 0.202 and 0.466 Å, respectively, to different sides of the mean plane of the C(1)C(2)C(3)C(6) atoms, which is a typical feature of such complexes [12, 14]. The Co-N interatomic distances are 1.888(2) and 1.882(2) Å and the Co-P distances are 2.3569(7) Å. The Co–P bond lengths in II differ by 0.1 Å from these bonds found in dioximes containing one coordinated PPh₃ molecule (e.g., the $[Co(DH)_2(PPh_3)(H_2O)]^+$ cation [16]) but are roughly equal to the bonds found in this type of complexes with two PPh₃ molecules [7, 12]. In the PPh₃ ligands of **II**, the P–C interatomic distances are 1.824(3)– 1.829(2) Å and the CPC bond angles are $100.4(1)^{\circ}$ -110.70(8)°. The interatomic distances (2.946-3.103 Å) between the carbon atoms of the PPh₃ phenyl groups and the oxygen atoms of the NioxH⁻ oxime groups suggest the formation of weak C-H-O intraion HB.

The Sb–F bond lengths in the $[SbF_6]^-$ anions of II (1.883(2)–1.895(2) Å) do not differ from those found in I. Although the outer-sphere anion in II does not form strong inter-ion HB as in I, it makes a considerable contribution to the packing of components in the crystal, as all fluorine atoms are involved in weak interion HB, C(Ph)–H…F (C…F 3.319–3.381 Å) (Fig. 4).

In the crystal structure of I and II, electrostatic interactions between the complex cations and anions

D–H…A contact	Distance, Å			DHA angle	Coordinates				
	D–H	Н…А	D…A	DTTA aligie	of A atoms				
Ι									
O(2)-H(1)···O(1)	0.96	1.59	2.518(3)	160	-x, -y+1, -z+2				
$N(3)-H(1)\cdots O(1w)$	0.91	2.08	2.984(3)	177	<i>x</i> , <i>y</i> , <i>z</i>				
N(3)-H(2)…F(2)	0.91	2.09	2.990(3)	171	<i>x</i> , <i>y</i> , <i>z</i>				
$O(1w)-H(1)\cdots F(1)$	1.01	2.19	3.101(3)	150	x, y + 1, z				
O(1 <i>w</i>)-H(1)····O(2)	1.01	2.26	2.934(2)	123	<i>x</i> , <i>y</i> , <i>z</i>				
п									
O(2)-H(1)···O(1)	0.82	1.76	2.539(2)	159	-x+1, -y, -z				

 Table 3. Geometric parameters of intra- and intermolecular hydrogen bonds in I and II



Fig. 1. Structure of the components of I and atom numbering.

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Fig. 2. Fragment of crystal structure I.



Fig. 3. Structure of the components of II and atom numbering.



Fig. 4. Fragment of crystal structure II.

are supplemented by inter-ion HB, including weak $C-H\cdots F$ bonds.

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